EXHIBIT F

Source Apportionment of Polychlorinated Biphenyls in Atmospheric Deposition in the Seattle, WA, USA Area Measured with Method 1668

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Abstract

Atmospheric deposition can be an important pathway for the delivery of toxic polychlorinated biphenyls (PCBs) to ecosystems, especially in remote areas. Determining the sources of atmospheric PCBs can be difficult, because PCBs may travel long distances to reach the monitoring location, allowing for a variety of weathering processes that may alter PCB fingerprints. Previous efforts to determine the sources of atmospheric PCBs have been hampered by the electron capture detection methods used to measure PCBs. In this work, EPA method 1668, which is capable of measuring all 209 congeners, was used to measure PCBs in bulk atmospheric deposition at seven locations in the Green-Duwamish River watershed in and near Seattle, WA. Analysis of this data set via Positive Matrix Factorization allowed the identification of six factors that represent PCB sources. Four factors, representing approximately 88% of all PCB mass, are strikingly similar to unweathered Aroclors, suggesting minimal weathering during transport and/or local PCB sources at some sites. A fifth factor contained virtually all of the PCB 11 mass and represents PCBs from pigments. It explained approximately 39% of the Toxic Equivalency Quotient in the atmospheric deposition samples. The remaining factor contained non-Aroclor PCBs and may be related to silicone.

Atmospheric deposition can be an important pathway for the delivery of persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs), to ecosystems, especially in remote areas (Choi et al. 2008; Hung et al. 2005, 2010; Li et al. 2012; Simcik et al. 1997; Totten et al. 2004, 2006). Determining the sources of atmospheric PCBs can be difficult, because PCBs may travel long distances to reach the monitoring location (Choi et al. 2008; Hung et al. 2005, 2010), allowing for a variety of weathering processes, such as volatilization, condensation, and reaction with hydroxyl radicals (Anderson and Hites 1996; Totten et al. 2001), which may alter PCB fingerprints during transport.

Source apportionment of the PCB signal is only possible when many PCB congeners are measured and is most

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successful when the methods to measure PCBs are the most sensitive and accurate available. The most sensitive method in the United States is the EPA method 1668 (U.S. EPA 1999; U.S. EPA 2010), which uses high-resolution mass spectrometry and is capable of measuring all 209 PCB congeners and of resolving the dioxin-like congeners, but this method has not been widely used in atmospheric deposition studies. Two of the main atmospheric deposition monitoring networks in the United States—the Integrated Atmospheric Deposition Network (IADN) in the Great Lakes (Basu et al. 2009; Rodenburg and Meng 2013; Sun et al. 2007) and the Delaware Atmospheric Deposition Network (DADN) in New Jersey, Pennsylvania, and Delaware (Praipipat et al. 2017)—have primarily used electron capture detection (ECD) methods to measured approximately 90 PCB congeners that are typically found in the Aroclor PCB formulations produced in the United States by the Monsanto Company. Several studies have attempted to apportion atmospheric PCB sources using data from these two networks (Du et al. 2009; Praipipat et al. 2017; Rodenburg and Meng 2013). These studies have generally focused on the gas phase and have observed PCB fingerprints that resemble low molecular weight PCB formulations, such as Aroclor 1242, as well as fingerprints that resemble weathered Aroclors. Notably, these source apportionment studies have suggested that PCB concentrations in

the gas phase are not displaying uninterrupted declines in Chicago, IL, and two cities in New Jersey, suggesting that identifying the PCB sources is necessary to implement strategies to eliminate them. The ECD-based methods used in these studies introduce significant limitations: non-Aroclor PCBs could not be studied because they were not measured, but studies in both urban (Hu et al. 2009) and remote (Choi et al. 2008) areas have observed the non-Aroclor congener PCB 11 in the gas phase. Also, incinerators can serve as non-Aroclor sources of PCBs and are notable for producing dioxin-like PCB congeners (Jansson et al. 2011), but again these sources are difficult to identify using ECD methods, because they often cannot resolve the dioxin-like congeners from other PCB congeners.

In this work, data from the Lower Duwamish Waterway (LDW) Source Control Bulk Atmospheric Deposition Study and its Supplement (King County 2013, 2015) were used to apportion PCB sources in samples from Green-Duwamish watershed, which is home to the Seattle, WA, metropolitan area. In these studies, PCB congeners were measured in bulk atmospheric deposition (King County 2013, 2015) at seven locations throughout the Green-Duwamish watershed (Fig. 1). The purpose of this study was to use this high-quality data set to apportionment PCBs sources in the Green-Duwamish watershed. Specifically, we sought to quantify Aroclor versus non-Aroclor PCB sources and to examine the differences in PCB sources between rural, suburban, and rural locations.
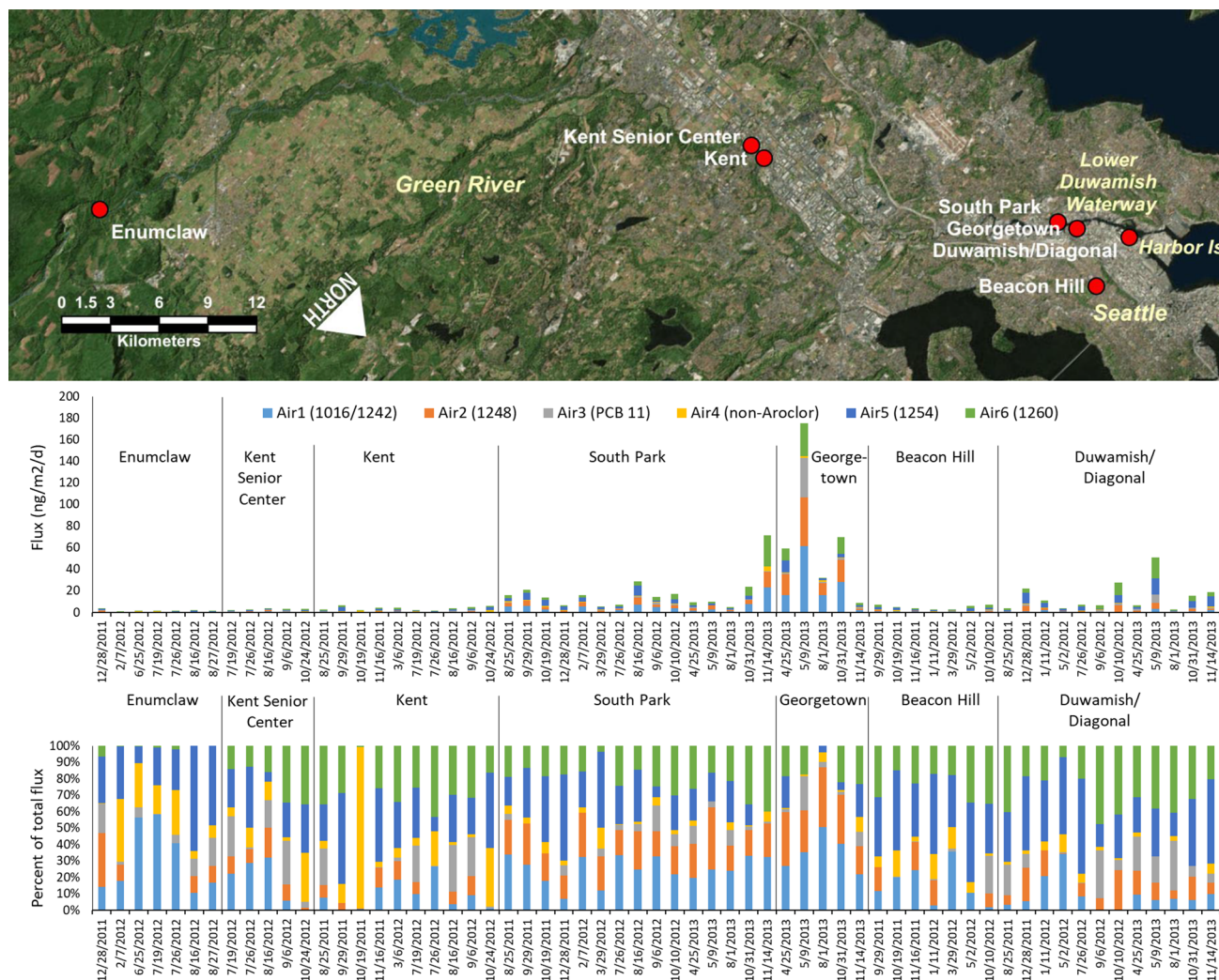
Fig. 1 Map of study area (top panel) showing sampling cites (red dots, white labels) and other geographic features (yellow labels). The middle panel shows the factor scores in units of flux (ng m^{-2} day^{-1}), while the lower panel shows the factor scores as a percent of total PCBs in each sample

Methods

The LDW Source Control Bulk Atmospheric Deposition Study and its supplement (King County 2013, 2015) were conducted to compare the measurements of bulk deposition (dry particulates and precipitation) at a seven stations (Fig. 1) in areas of different land uses within the Green-Duwamish River watershed and to provide information to assist in understanding atmospheric sources to the LDW Superfund site. The Duwamish/Diagonal station represents industrial and urban land uses. The South Park and Georgetown locations represent a mix of suburban, industrial, and residential land uses. These two sites are positioned relatively centrally in the LDW corridor, approximately 4-km apart, and on opposite sides of the Duwamish River. Georgetown also lies within the LDW study area. The Beacon Hill station represents urban residential land use. The Kent and Kent Senior Center stations represent suburban and commercial land use, whereas the Enumclaw data represents rural and forestry land uses. Beacon Hill is also an EPA Pacific Northwest urban scale air toxics station. The other sites are part of the Puget Sound Clean Air Agency's regional network of air quality monitoring stations (King County 2013, 2015).

Sample Collection

Details of sample collection and analysis are available in the project reports (King County 2013, 2015). Briefly, dry and wet deposition were collected with a stainless steel funnel connected to a 4-L amber glass sample bottle by polytetrafluoroethylene (PTFE) tubing. Larger diameter (45 cm) funnels were deployed with the organics samplers during the dry (summer) season, whereas smaller diameter (23 cm) funnels were deployed during the wet (winter) season. This funnel size change was necessary to collect sufficient mass for analysis in the dry season yet prevent overflowing the collection vessels in the wet season. The first phase of the study collected atmospheric deposition between July 27, 2011 and October 24, 2012 (King County 2013). The supplemental study collected samples between April 25, 2013 and November 14, 2013 (King County 2015). The deployment period ranged from 7 to 30 days and was not continuous at all sites due to budget constraints. Table S-1 of supporting information gives details about each sample. PCB concentrations were measured in the bulk deposition samples via EPA methods 1668A and 1668C by Axys Analytical Services (British Columbia, Canada). This method allows the detection of all 209 PCB congeners in about 169 peaks. Data were blank corrected by the contract laboratory before being entered into the database. Concentration (C in ug L^{-1}) was converted to flux (F in ng m^{-2} day^{-1}) via the following formula:

$$F = \frac{C \cdot \left(V_{\text{rain}} + V_{\text{rinse}}\right)}{A \cdot t}$$

where V_{rain} is the volume of rain collected, V_{rinse} is the volume of the water used to wash deposited contaminants off the funnel into the collection bottle at the time of collection, A is the surface area of the collection funnel, and t is the time in days. The measurement of flux instead of concentration should not affect the fingerprinting of PCBs sources. Atmospheric deposition networks that measure concentration instead of flux must convert those concentrations to fluxes by multiplying by a deposition velocity that is the same for all PCBs in a given sample (Hillery et al. 1998; Totten et al. 2004). Thus, the conversion from concentration to flux does not affect the relative concentrations of the PCB congeners and therefore should have no effect on the fingerprinting.

Data Analysis

The goal of the PMF analysis was to understand the sources of as much of the PCB mass and Toxic Equivalency Quotient (TEQ) as possible. Since only 64 samples were available, all 64 were included in the model without averaging of the three samples analyzed in duplicate. The final data matrix therefore contained 64 samples and 69 peaks. Rules for inclusion of analytes (PCB peaks) in the model were as follows: for dioxin-like congeners, a minimum of 19 detections across the 64 samples was required. This rule allowed the inclusion of 10 of the 12 dioxin-like PCB congeners: PCBs 77, 105, 114, 118, 123, 126, 156 + 157, 167, and 189. Two dioxin-like congeners were omitted, because they were rarely detected; PCB 169 was detected in only 1 sample, whereas PCB 81 was detected in 8 of the 64 samples. For all other PCB peaks, a minimum of 35 detections was required. This allowed the inclusion of a total of 69 peaks representing 108 congeners, 12 of which were dioxin-like, out of the total of 159 peaks in which the 209 congeners were measured. These 69 peaks represent 89% of the PCB mass (i.e., the other 90 peaks represent the other 11% of the mass). As a result of this data censoring, 21% of the $64 \times 69 = 4416$ data points submitted for PMF analysis were below detection.

Fluxes of individual congeners in ng m^{-2} day^{-1} were used to apportion PCB sources using the Positive Matrix Factorization (PMF2) software of Paatero and Tapper (1994). Details of the construction of the input data sets and criteria used to identify the optimal number of factors are presented in the supporting information. The resolved factors were

compared with the Aroclor congener patterns measured by Rushneck et al. (2004) using method 1668.

Results and Conclusions

Fluxes of the sum of PCBs (Σ_{209}PCBs) were lowest (averaging 1.1 ng m^{-2} day^{-1-}) at the most remote site, Enumclaw, and highest at the most urban site, South Park (averaging 16.9 ng m^{-2} day^{-1}) (King County 2013, 2015). These fluxes are relatively low compared with those measured by the DADN circa 2005. In urban Camden, NJ, gas absorption alone was estimated to be 270 ng m^{-2} day^{-1}, and dry particle plus wet deposition equaled 95 ng m^{-2} day^{-1}. The lowest deposition flux measured by the DADN was observed at rural Alloways Creek, where the gas absorption was estimated to be 12 ng m^{-2} day^{-1}, and dry particle plus wet deposition was 2.5 ng m^{-2} day^{-1} (Totten et al. 2006). Data from the IADN from 2015 were used to calculate that the atmosphere delivers 120 ± 68 kg year^{-1} of total PCBs to Lake Michigan via gas absorption, 25 ± 3 kg year^{-1} via wet deposition, and 17 ± 12 kg year^{-1} via dry deposition (Guo et al. 2017). Dividing by the surface area of Lake Michigan of 57,800 km^2, these loads correspond to a flux of approximately 7.7 ng m^{-2} day^{-1} for all three modes of deposition combined. Note that both the DADN and IADN measured PCB concentrations in the particle and precipitation phases and estimated the rate of deposition from these concentrations. In contrast, PCBs were measured in bulk deposition (combined wet and particulate) in the Green-Duwamish watershed, i.e., flux was measured directly.

PMF Results

PMF analysis of the atmospheric deposition data set produced six factors (see Supporting Information for details on the criteria used to determine this). These are denoted as Air1 through Air6. Four factors resemble the four main Aroclors (1242, 1248, 1254, and 1260) and two factors (Air3 and Air4) are not similar to any Aroclors but contain non-Aroclor congeners (see below).

Note that throughout this paper we express the importance or weighting of each factor in terms of how much of the mass in the data set the PMF model attributes to each factor. This is a convenient number to cite because it is exact and is an output of the PMF model. It is important to remember that this is only an accurate estimate of the importance of various sources if we assume that the sample set is truly representative of environmental conditions in this region. This assumption is particularly tricky in the present case, because the total atmospheric deposition of PCBs to the Green-Duwamish watershed is a function of the bulk deposition flux multiplied by the surface area over which that

flux applies. For example, the flux at Enumclaw is the lowest among the seven sites, but it is likely that this flux applies over a very large proportion of the 1250 km^2 watershed area, wherever it is forested and largely undeveloped. Conversely, the flux at Georgetown is the highest, but it presumably only applies over a very small area of central Seattle, perhaps only a few square kilometers.

Non-Aroclor Factors

Air3 has an average molecular weight (MW) of 293.0 and is dominated by PCB-11 (30% of the factor fingerprint). This factor explains 99.8% of all the PCB-11 in the data set. Notably, although PCB-209 is just 0.5% of the factor fingerprint, Air3 explains 8.5% of the mass of PCB-209 in the data set. Air3 also explains 10% of the mass of PCB-206 and 3% of the mass of PCB-208. Thus, Air3 explains a significant portion of the mass of all four of these congeners that are thought to be associated with non-Aroclor sources. PCB 11 is mostly absent from the Aroclors but has been found in a variety of pigments (Litten et al. 2002; Rodenburg et al. 2010, 2015; Rushneck et al. 2004; The Japanese Ministry of Economy Trade and Industry (METI) 2013). PCB 209 has been associated with non-Aroclor sources, such as titanium dioxide (Du et al. 2008; Gamboa et al. 1999) and phthalocyanin green (Hu and Hornbuckle 2010) pigments. However, PCB 209 also is present in some Aroclors, such as 1268, 1270, and 1272 (Hermanson et al. 2016; Rushneck et al. 2004).

Overall, Air3 explains 8.5% of the PCB mass in the data set. Because Air3 includes some Aroclor congeners, we also examined the importance of these four congeners separately (i.e., without factor analysis). PCBs $11 + 206 + 208 + 209$ comprise 9.4% of the PCB mass in the data set. They range from 1.1 to 29% of PCB mass in individual samples. These four PCB congeners can be produced during incineration of municipal solid waste (Jansson et al. 2011). However, this process also tends to produce all of the dioxin-like PCB congeners, with PCBs 77, 81, 105, $156 + 157$, and 189 being particularly abundant in fly ash from such incinerators (Jansson et al. 2011). These congeners are not particularly abundant in Air3, and the Air3 fingerprint (Fig. 2) does not resemble those measured in fly ash (Jansson et al. 2011). In addition, there are no incinerators located in Washington State west of the Cascade mountain range, where the monitoring sites were located. Thus it is unlikely that Air3 represents PCBs from incineration.

Air4 has an average MW of 325.17 and is dominant (i.e., more than 94% of total PCBs) in one sample analyzed in duplicate from the Kent sampling station. This sampling station was located approximately 250 feet from a local commuter rail line, which supports nine northbound and nine southbound trains that stop at this
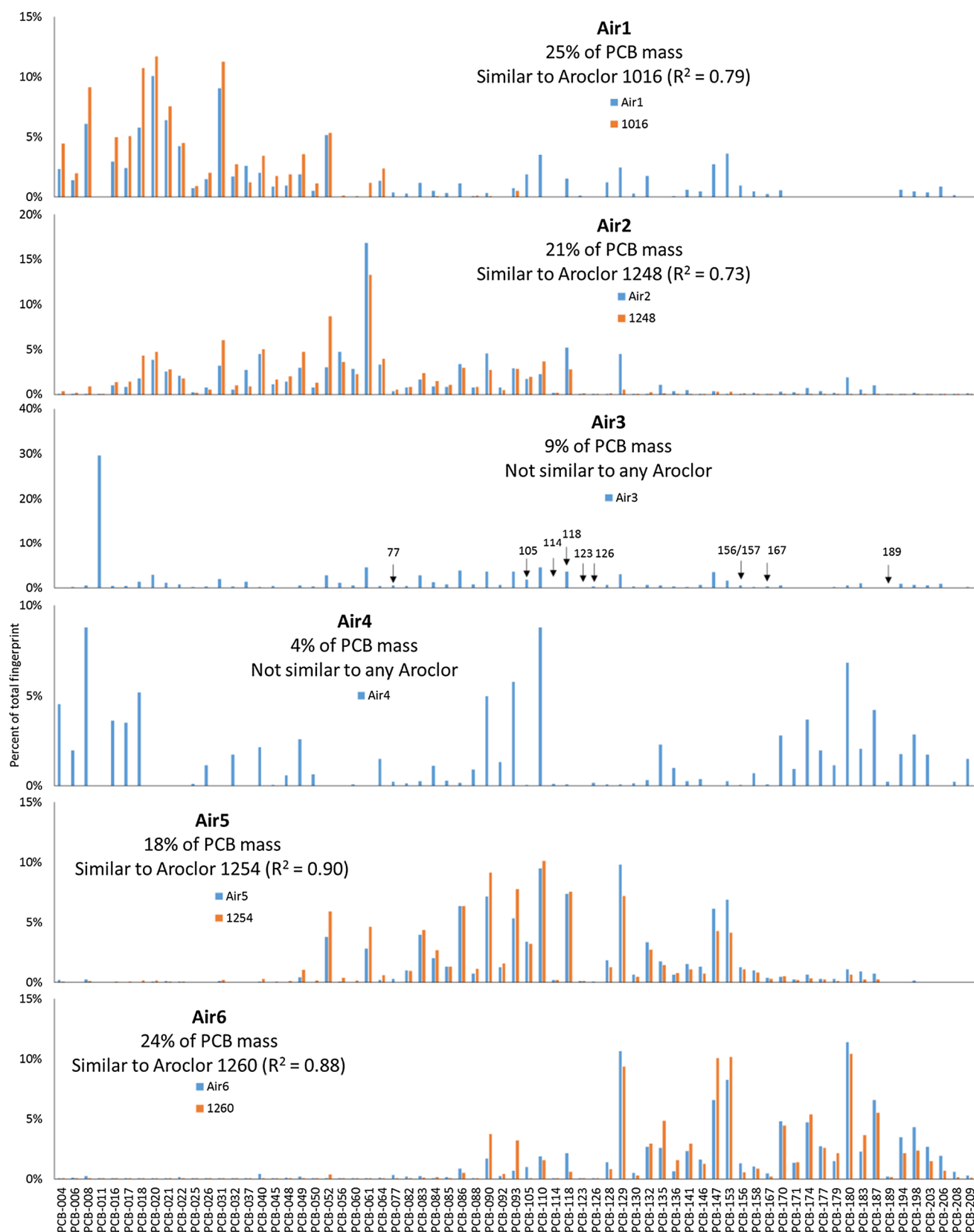
Fig. 2 Fingerprints of the six factors resolved from PMF2 analysis of the atmospheric deposition data set compared to their best-match Aroclors. Arrows indicate dioxin-like congeners

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location on weekdays. In addition, Amtrak passenger trains and freight trains use this same rail line to pass through Kent. The dominant congeners in this factor are PCBs 4, 8, 16, 17, 18, and 49. These congeners have been observed in silicone products (Anezaki and Nakano 2015; Perdih and Jan 1994). They can be introduced into samples via the use of silicone products such as rubber and caulk (Anezaki and Nakano 2015). Thus, Air4 may result from the use of these products at or near the sampling site or may represent blank contamination associated with use of these products during sampling or within the contract laboratory. Air4 contains 1.5% PCB 209 and explains 32% of the mass of PCB 209 in the data set. Although this congener has not been reported in silicone, titanium dioxide often is used to create the white color in silicone caulks and sealants (a Google search finds hundreds of products containing titanium dioxide in silicone). Air4 comprises just 3.8% of the mass in the data set.

Aroclor Factors

Factor Air1 has an average molecular weight (MW) of 287.6 and probably represents both Aroclors 1242 and 1016, but it better resembles Aroclor 1016, probably because Aroclor 1016 is a distillation of Aroclor 1242 in which many of the higher molecular weight congeners have been removed (Erickson 1997). This may suggest that Air1 represents low molecular weight Aroclor formulations that have vaporized, because vaporization is similar to distillation. Aroclor 1242 represents approximately 52% of U.S. Aroclor production from 1957 to 1977 versus just 13% for Aroclor 1016 (Brown 1994). Air1 contains more of the higher molecular weight congeners than either Aroclor 1016 or 1242. This may represent mixing of sources during atmospheric transport.

Air2 has an average MW of 304.95 and is similar to Aroclor 1248 ($R^2 = 0.73$) but contains some higher molecular weight congeners. Again, this may indicate mixing of PCB sources during transport.

Air5 has an average MW of 339.0 and strongly resembles Aroclor 1254 ($R^2 = 0.90$). Air6 has an average MW of 378.43 and strongly resembles Aroclor 1260 ($R^2 = 0.88$). These factors may represent PCBs that have never been in the gas phase because they display minimal mixing or weathering. Instead, they were probably present on dust or soil particles that became airborne and then deposited at the monitoring site. Because particles are scavenged more efficiently out of the atmosphere than gas-phase compounds, contaminants that travel with the particle phase generally do not travel as far as gas-phase contaminants and, therefore, are more likely to be of local origin (MacLeod and Mackay 2004).

Weathering of PCB Sources

The striking feature of the Green-Duwamish data set is how closely the congener patterns resemble unweathered Aroclors. This is due in part to the fact that most of the samples were collected at urban/suburban sites. This suggests minimal weathering during transport to the urban/suburban sites, which are near sources and therefore require relatively little transport. These results suggest that the lower MW Aroclors undergo more weathering via vaporization, reaction (Anderson and Hites 1996), and mixing during transport than the higher MW formulations, which probably remain bound to particles and never enter the gas phase. Nevertheless, it is notable that none of the factors resembles a vaporized Aroclor: multiplying the Aroclor congener patterns by the vapor pressures of the congeners results in profiles that do not resemble any of the factors. This may suggest that most of the PCBs in the bulk deposition are associated with particles and never entered the gas phase.

The agreement between the model-predicted factor fingerprints and the measured fingerprints was best (highest R^2) at the sites with the highest fluxes. For example, at Georgetown, the average ($\pm$ standard deviation) agreement (R^2) was 0.981 ± 0.008, while at Enumclaw, the R^2 averaged 0.530 ± 0.336. This may reflect alteration of the PCB fingerprints during transport, but it also may simply reflect the difficulty of accurately quantifying PCBs near the detection limit, because individual samples with the lowest fluxes also displayed the weakest agreement between the measurements and the model predictions. This trend of worse model predictions at the most remote sites bolsters our hypothesis that the PCB sources are local to the more impacted sites, but undergo weathering during transport to the remote sites.

Spatial Distribution of PCB Sources

Previous studies of atmospheric deposition have noted that the PCB congener pattern has a higher average MW in urban areas and lower MW in rural areas. This has been called the "urban fractionation effect" and is thought to occur because lower molecular weight congeners have higher vapor pressures and therefore less of their mass is in the particle phase, allowing them to travel farther (Gingrich and Diamond 2001; Harner et al. 2004). The phenomenon is observed in this data set and supports our hypothesis that the higher MW PCBs travel via particles, keeping their congener patterns relatively intact and therefore are not transported as far as the lower MW formulations, which are primarily in the gas phase where vaporization and photochemical reactions are more likely to alter their congener patterns. In Fig. 1, the monitoring sites are ordered from south to north, which roughly corresponds to rural to urban. Note how the Enumclaw samples have almost none of the factor with the highest

average MW (Air6 representing Aroclor 1260), while the urban sites, such as Duwamish/Diagonal and Beacon Hill, have very little of the factor with the lowest average MW (Air1 representing Aroclors 1016 and 1242). This pattern is not observed at the two sites with the highest flux: South Park and Georgetown. This may indicate that local sources of lower MW PCB formulations exist at these two sites. This is in agreement with their urban/industrial settings and is consistent with our hypothesis above that the close agreement between the PMF factor fingerprints and the unweathered Aroclors indicates local sources near these monitoring sites. Similar spatial patterns are observed when the samples are examined synoptically (see supporting information Fig. S-1). For any given sampling event, the urban samples usually contain higher fractions of the factors with the higher average MWs.

Comparison to Other Locations

Comparing the results of this study with data from other atmospheric deposition networks is complicated by differences in methodology. Previous studies have apportioned sources of PCBs in the atmosphere using data from the two networks described in the introduction: the IADN and the DADN. There are two important differences between the data collected by these networks and the present data set. First, source apportionment of the IADN and DADN has focused only on gas phase samples collected over 24-h periods (Praipipat et al. 2017; Rodenburg and Meng 2013), while the present work collected bulk deposition (i.e., precipitation and particles) over several days. One important consequence of this collection method is that the temperature dependence of any of the factor fingerprints from the present work are difficult to assess. Second, IADN and DADN measured PCBs using ECD on a DB-5 column, whereas the present study used high-resolution mass spectrometry on an SPB-octyl column. This can lead to differences in congener patterns based solely on the analytical method. Also, the ECD methods did not measure many of the non-Aroclor congeners, such as PCBs 11 and 209.

Keeping these differences in mind, we can make a few general observations about the various data sets. PCB factor fingerprints in the Green-Duwamish data set closely resemble unweathered Aroclors. Factor analysis of PCB fingerprints in gas-phase air samples collected in Chicago, IL (Rodenburg and Meng 2013), as well as Camden and New Brunswick, NJ (Praipipat et al. 2017) isolated fingerprints that were less similar overall to the Aroclors. However, these earlier studies did suggest that at least 75% of the gas-phase PCBs in these areas were attributable to identifiable Aroclors (Praipipat et al. 2017; Rodenburg and Meng 2013). In these cities, PCBs were measured in the gas phase (not deposition); therefore, the congener patterns would be less likely to resemble Aroclors due to the vaporization process.

Factor analysis of PCB fingerprints in gas-phase air samples collected in Chicago, Camden, and New Brunswick yielded one factor at each location that probably represent a highly weathered mixture of several Aroclors. In the present work, all of the factors that resembled Aroclors were strongly similar ($R^2 > 0.7$) to one specific Aroclor, indicating minimal weathering. Any weathering was more evident in the relatively poor model fits at the most remote site (Enumclaw). This may be an artifact of the dominance of urban sites in this data set, or it may reflect the fact that most of the PCBs captured by the bulk deposition method are bound to particles. Because they never entered the gas phase, they had less opportunity to undergo weathering.

At all three locations in Chicago and New Jersey, the factors representing weathered mixtures of sources were strongly temperature-dependent, and this was interpreted to mean that the factors were associated with secondary PCB sources (i.e., PCBs that were emitted directly to the atmosphere long ago have redeposited to surfaces, such as soil, and then revolatilized at high temperatures). This process allows many PCB sources to mix, yielding a congener pattern that is not similar to any one Aroclor (Praipipat et al. 2017; Rodenburg and Meng 2013). As noted, it is difficult to assess the temperature dependence of the factors in the present work due to the collection method. However, Fig. 1 demonstrates that the factor scores (fluxes) do not display the kind of seasonality that would be expected if temperature was driving PCB concentrations in the bulk deposition. High fluxes are just as common in winter as in summer. Our observation above that most of the PCB burden in the bulk deposition is associated with particles might suggest that bulk deposition fluxes should be greater in the rainy (winter) season than in the drier (summer) season. However, the lack of seasonality suggests that this is not necessarily true. The bulk deposition fluxes appear to vary randomly without regard to temperature or precipitation.

Dioxin-like Congeners

Toxic equivalency quotient (TEQ) values were calculated for the dioxin-like congeners using the World Health Organization's 2005 Toxic Equivalency Factor (TEF) values (Van den Berg et al. 2006). The distribution of the mass of dioxin-like congeners (DLCs) is similar to the distribution of the total PCB mass (Table 1), but the distribution of TEQ is very different. Air3, which contains the non-Aroclor congener PCB 11 and therefore may derive from pigments, contains the most TEQ, due primarily to the distribution of the mass of PCB 126. The PMF model ascribes 40% of the PCB 126 mass to Air3. However, this should be interpreted with caution, because PCB 126 was the congener with the weakest

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Table 1 Distribution of the mass and TEQ of PCB congeners across the six resolved factors

	Air1 (1016/1242) (%)	Air2 (1248) (%)	Air3 (PCB 11) (%)	Air4 (non-Aroclor) (%)	Air5 (1254) (%)	Air6 (1260) (%)
Percent of total PCB mass	25	21	8.5	3.8	18	24
Dioxin-like congeners, distribution of mass						
PCB-077 (TEF = 0.0001)	26	21	14	2	14	22
PCB-105 (TEF = 0.00003)	26	19	8	0	34	13
PCB-114 (TEF = 0.00003)	5	36	11	4	37	6
PCB-118 (TEF = 0.00003)	10	30	9	0	37	14
PCB-123 (TEF = 0.00003)	48	0	15	1	35	0
PCB-126 (TEF = 0.1)	5	0	40	10	24	22
PCB-156 + 157 (TEF = 0.00003)	29	0	5	0	28	37
PCB-167 (TEF = 0.00003)	24	0	11	1	26	38
PCB-189 (TEF = 0.00003)	9	5	10	11	5	60
Sum of 10 DLC mass	18	21	8.9	0.5	33	18
Percent of TEQ						
All 10 DLC congeners	5	1.0	39	10	24	22
Nine congeners (excluding PCB 126)	19	22	9.2	0.64	31	18

Note that PCB 126 was not well described by the PMF model

correlation between the measured and model-predicted fluxes ($R^2 = 0.55$ after removal of one obvious outlier; see supporting information for more details). The poor fit is due in part to the large proportion of samples in which PCB 126 was not detectable (36 of 64 samples). There is some reason to believe that PCB 126 could be associated with pigments: Litten et al. (Litten et al. 2002) observed PCBs 11 (3,3′-dichlorobiphenyl), 77 (3,3′,4,4′-tetrachlorobiphenyl), and 126 (3,3′,4,4′,5-pentachlorobiphenyl) in waste from a pigment manufacturer. This data set therefore provides some indication that pigment sources may contribute significantly to the total TEQ in atmospheric deposition. However, if PCB 126 is excluded from the calculation of TEQ due to the low accuracy of the PMF model for this congener (last line in Table 1), the TEQ distribution is more similar to the distribution of mass, and Air3 contributes just 9.2% of total TEQ. Thus more work is needed to better understand the sources of PCB-associated dioxin-like toxicity in atmospheric deposition.

The PMF model indicates that Air4, which may represent PCBs from silicone, is responsible for approximately 10% of the total TEQ. Again, this should be interpreted with caution, because the TEQ is due almost entirely to PCB 126, which is not well described by the model. Neither Perdih and Jan (1994) nor Anezaki and Nakano (2015) reported detecting PCB 126 in silicone products.

The heavier Aroclors (1254 and 1260) comprise approximately half of the total TEQ in the atmospheric deposition. We have argued that these Aroclors do not travel as far as the lower MW formulations and are more likely to be in the particle (aerosol) phase, suggesting that efforts to control TEQ in atmospheric deposition should focus on the remediation of contaminated soil at sites known to possess PCB contamination, especially if higher MW Aroclors were used at those sites. Because the higher MW Aroclors are less abundant at the remote sites, Air3 (PCB 11/pigment) is responsible for a greater proportion of the TEQ in rural/forested areas, which comprise much of the watershed of the Green-Duwamish River.

This study suggests that relatively unweathered Aroclors are the main PCB sources in atmospheric deposition, which suggests that PCB sources are relatively local, especially in urban/industrial areas. In more locations, secondary and non-Aroclor PCB sources are important. Because the sources of dioxin-like TEQ may be very different from the sources of PCB mass, efforts to control atmospheric deposition must choose whether to focus on PCB mass or TEQ.

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Source Apportionment of Polychlorinated Biphenyls in Atmospheric Deposition measured with Method 1668

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Details of sample collection

Details of sample collection are quoted from the deposition study documents: [1]

> "Sampling systems were constructed based on the design described in the project SAP [sampling and analysis plan] and consisted of a wood-framed structure supporting up to four collection funnels that each drain directly into a sample bottle. Collection funnels sat approximately six feet above the ground or roof, depending on the station. Each sampling system was comprised of one or two organics samplers, and if identified in study design, a metals sampler and a mercury sampler. Organics samplers collected dry and wet deposition with a stainless steel funnel connected to a 4L amber glass sample bottle by Teflon® tubing. The sample bottle was protected from light by a wooden

enclosure. One organics sampler collected samples for PCB and dioxin/furan congener analyses and a second organics sampler collected samples for PAHs analysis. Mercury and metals samplers collected wet and dry deposition with a plastic funnel (high-density polyethylene) connected to a 2 L fluoropolymer sample bottle.

Larger diameter (45 cm) funnels were deployed with the organics samplers during the dry season (July 2 through September 5) while smaller diameter (23 cm) funnels were deployed during the wet season. Differences in funnel size were necessary to collect sufficient mass for analysis in the dry season yet prevent overflow in the collection vessels during the wet season.

Carboys, funnels, and other sampler components were cleaned using: (1) laboratory detergent; (2) a deionized water rinse; and (3) an acetone rinse. The collection bowl and attached tubing were cleaned at King County Environmental Laboratory (KCEL) prior to deployment. The 4 L amber glass sample bottles for PCB and dioxin/furan congener samples were proofed and provided by AXYS Analytical Services (AXYS). KCEL pre-cleaned similar 4 L amber glass bottles for PAH samples. Sample bottles for metals and mercury analysis were cleaned prior to use by KCEL using the following steps: fill each bottle with 1:1 nitric acid and soak in a hot water bath for 24 hours, rinse with reagent water, then repeat these two steps and fill the bottle with 1% hydrochloric acid instead of nitric acid.

Samples were collected by consecutively targeting 2- to 4-week collection periods for PAHs, metals and mercury. Because a limited number of samples were collected for PCB

and dioxin/furan analyses, the collection periods for these samples were not necessarily consecutive. Shorter collection periods occurred during the wet season for all samples (i.e. October–May) to reduce risk of sample overflow. Longer collection periods were employed during the dry season (i.e. June–September) to maximize atmospheric deposition collection.

At the time of retrieval, the rainfall level or "deposition volume" in each collection vessel was recorded on the sample container using lab tape and a marking pen. After marking the water level on the sample container, a known quantity of reverse osmosis (RO) water was used to rinse dry particulates from the funnel into each collection vessel (i.e. rinse volume). Removal of particulates was enhanced by brushing the funnel during rinsing with a natural hair, acetone-cleaned paintbrush. Following this step, the funnel was disconnected, and the collection vessel was capped and stored on ice during return to KCEL. The rinse volume and funnel surface area were recorded on field sheets and entered along with deposition volume into the King County Laboratory Information Management System (LIMS).

The organics sampler for PCBs and dioxins/furans was removed from the field between sampling periods and re-cleaned and stored at KCEL before redeployment. Organics sampler units for PCBs and dioxins/furans were dedicated to each station and remained with their assignments throughout the study."

Details of PCB analysis

PCB analysis was performed via method 1668C[2] by Axys Analytical Services (now SGS AXYS) in British Columbia, Canada. Detection limits depended on the sample collection period and the volume of rain. The highest congener-specific detection limit was 139 ng m^{-2} d^{-1}, which occurred during the shortest deployment (i.e. 7 days). The lowest detection limit was 0.00011 ng m^{-2} d^{-1}, which occurred during the longest deployment of 30 days.

Additional details of PCB analysis quality assurance and quality control (QC) are quoted from the deposition study documents: [1]

> "PCBs and dioxin/furan data were validated to Level III by LDC [Laboratory Data Consultants]. Level III validation includes verification of custody, holding times, reporting limits, sample QC and QC acceptance criteria, and frequency of QC samples, instrument performance checks, along with initial and routine calibration checks…

> For PCBs, method blank contamination above method specifications was detected in all batches. One or more mono or di-chlorinated PCB congeners were detected in most method blanks. Several method blanks had detections across the entire PCB homolog range. Method blanks had as few as none and as many as 28 detected PCB congeners. Under this high resolution method that quantifies 209 PCB congeners with several co-elutions, it is common to detect some congeners in method blanks. Environmental sample detections were qualified as non-detect by the contract validator whenever sample concentrations were within five times the method blank concentration. This potentially resulted in some low bias for congeners detected above the method blank concentration but within five times the method blank.

Laboratory duplicate results were within method specifications for all but a few PCB congeners. RPD between laboratory duplicates are specified by the SAP to be plus or minus 50%. LDC applied this when both the parent and lab duplicate results were greater than five times the LMCL [lowest method calibration limits]. For sample L57717-5 and its duplicate RPDs [relative percent differences] for PCB 206 and 208 were 51.4 and 50.5 percent. These congeners were flagged as estimated in this sample due to this slight method performance issue.

Internal standards for PCB analysis were within method specifications with some exceptions. The internal standard 13C PCB-4 in sample L58204-9 fell below allowable recovery limits of 25 to 150% with 22.1% recovery. This resulted in flagging the mono and dichlorinated biphenyls which are quantified relative to this standard's recovery as estimated. Detects of PCB congeners 4 through 14 and associated total dichlorinated biphenyls were qualified as "J" or estimated while non-detected congeners were qualified as "UJ" for estimated detection limits.

Numerous dioxin/furan and PCB congeners were qualified by the analytical laboratory as "K" which means that not all identification and qualification criteria were met for these compounds. The maximum potential concentration is reported for "K" flagged congeners. These analytes were qualified as non-detects by the validator according to the EPA Region 10 validation guidelines."

PMF model details

The PMF2 model requires three input data sets pertaining to the concentration, limits of detection (LOD), and uncertainty. In this case, the LODs provided by the contract lab were in units of concentration, not flux, and since the conversion of concentration to flux was not a constant, it was necessary to estimate the detection limits from the lowest detected flux for all congeners in a homolog across each sample. Note that the flux values were blank corrected by the laboratory before reporting. In some cases, especially for the nona- and deca-PCB homologs, there are a small number of congeners per homolog, and all of them were detected at high concentrations. In those cases, a reasonable LOD was inferred from the nearest homolog or from a similar sample from the same study. For the concentration (in this case flux) matrix, values below detection were substituted with a proxy value equal to a random number between zero and the estimated detection limit. In previous studies in which 1668 PCB data was analyzed via PMF2, uncertainty has been calculated as the relative standard deviation of the surrogate recoveries, which typically range from 10% to 35%. In the present work, surrogate recovery data was not available, so an uncertainty value was calculated for each congener from its relative percent difference (RPD) across three samples that were analyzed in duplicate. These uncertainty values ranged from 12% to 25%.

The final data matrix contained 64 samples and 69 peaks. These 64 samples include three samples that were analyzed in duplicate. Duplicates were averaged in the G-matrix after the PMF analysis was conducted so that the discussion and analysis of results does not 'double-count' the duplicates (see for example figure 2 and table 1). In this data set, 21% of the data points were below detection.

Selecting Optimal Number of Factors

All forms of factor analysis require the operator to identify the optimal number of factors, or source fingerprints, that adequately describe the data set.[3] The model was run for multiple cases, including varying assumptions of 3 to 7 factors, and the model was run 10 times at 10 different starting points (i.e., seed values) for each case. The output was used to identify which number of factors provides the optimal model solution. The current analysis used four main criteria to determine the 'best' number of factors. These criteria are similar to those proposed by Reff et al.[3], except that the comparison of the theoretical and calculated Q values was not relied upon to indicate the correct number of factors. This approach was rejected because the calculated Q depends on the uncertainty matrix, and there are many reasonable approaches to estimating uncertainty. When uncertainties are inaccurate, the theoretical and calculated Q values can differ substantially.[4]

- The first and most important criterion is that the factors must be interpretable and useful for source apportionment of contaminants. The six-factor model was interpretable, yielding four factors that resemble Aroclors and two factors that contain high proportions of non-Aroclor congeners.

- Second, the model solution should be stable. This is determined by running the model from many different starting points (i.e., seed values) for a given number of factors and determining whether all or most of them converge on the same solution. Similar solutions will have essentially the same Q value, G matrix, and F matrix. The relative standard deviation of 10 seed runs of the G matrix is used as an indicator of model stability (RSD¬G). As noted above, there are many ways to adjust the input matrix to attain a stable solution. The Q value is a function of the similarity between the

measured and modeled concentrations. All else equal, a lower Q value indicates a better

model fit. Thus, the seed run with the lowest Q value is used for all interpretations of

the model results. The six factor solution was stable: Six was the largest number of

factors that displayed a stable solution (i.e., 10 of the 10 runs of the 6-factor solution

agreed with each other, with an average RSD of the G matrix [RSDG] of just 5.1 percent).

- Third, the model solution should adequately describe the data (i.e., there should be

  reasonably close agreement between the measured and modeled concentrations). This

  is primarily evaluated by calculating the unadjusted R^2 value between the measured and

  modeled concentrations by analyte (i.e., PCB peak). In theory, requesting more factors

  should allow the model to produce a better fit to the measured data. Deterioration of

  the model fit when additional factors are requested is usually a sign of over-fitting (i.e.,

  too many factors have been requested). Six factors adequately described the data set:

  The agreement (R^2) between the measured and modeled concentrations was greater

  than 0.85 for 64 of the 69 peaks. The poorly described congeners included PCBs 206,

  208, and 209 with R^2 values of 0.60, 0.40, and 0.59, respectively. Removal of the four

  same outliers (from three different monitoring sites) caused these R^2 values to increase

  to greater than 0.75. PCBs 126 ($R^2 = 0.14$) and 146 ($R^2 = 0.50$) were both affected by one

  outlier. When this data point was removed, the correlation increased to 0.93 for PCB

  146, but only to 0.55 for PCB 126. PCB 126, which is dioxin-like, was generally not well

  described by the PMF model and this failure was not due to a small number of outliers.

  The failure may be related to the fact that PCB 126 was detected in only 28 of the 64

  samples.

- Fourth, a multiple linear regression of the G matrix versus the measured sum of analytes should yield positive and statistically significant coefficients for all factors. This criterion was met for the six-factor solution: The multiple linear regression yielded coefficients that were positive and significant ($p < 0.05$) for all six factors.

Table S-1. Samples by site and date of collection and sampling period duration. The results of the PMF analysis (Factor fluxes) are given in units of ng m^{-2} d^{-1}.

Site	end date	sampling period (days)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Beacon Hill	09/29/11	8	8.5E-01	1.1E+00	1.8E-04	4.7E-01	2.6E+00	2.3E+00
Beacon Hill	10/19/11	20	1.0E+00	1.1E-04	4.8E-03	8.2E-01	2.5E+00	7.4E-01
Beacon Hill	11/16/11	14	8.7E-01	6.2E-01	7.1E-03	1.0E-01	1.2E+00	8.2E-01
Beacon Hill	01/11/12	14	6.9E-02	3.6E-01	1.6E-02	3.6E-01	1.1E+00	4.0E-01
Beacon Hill	03/29/12	14	1.0E+00	3.1E-03	5.1E-02	3.7E-01	9.1E-01	5.0E-01
Beacon Hill	05/02/12	13	6.2E-01	9.1E-04	7.1E-03	3.9E-01	2.8E+00	2.0E+00
Beacon Hill	10/10/12	27	1.4E-01	5.7E-01	1.6E+00	9.0E-02	2.1E+00	2.5E+00
Duwamish/Diagonal	08/25/11	29	1.2E-01	2.1E-01	6.8E-01	6.0E-02	1.1E+00	1.5E+00
Duwamish/Diagonal	12/28/11	29	1.2E+00	4.5E+00	1.8E+00	4.9E-01	1.0E+01	4.1E+00
Duwamish/Diagonal	01/11/12	14	2.2E+00	1.7E+00	1.8E-02	5.9E-01	4.0E+00	2.2E+00
Duwamish/Diagonal	05/02/12	13	1.3E+00	9.5E-03	3.0E-02	4.0E-01	1.7E+00	2.5E-01
Duwamish/Diagonal	05/02/12	13	8.4E-01	7.1E-04	5.4E-02	1.6E-01	2.3E+00	3.4E+00
Duwamish/Diagonal	07/26/12	7	6.0E-01	5.6E-01	2.5E-02	3.9E-01	4.1E+00	1.4E+00
Duwamish/Diagonal	09/06/12	21	4.2E-03	4.6E-01	1.9E+00	1.5E-01	8.6E-01	3.0E+00
Duwamish/Diagonal	10/10/12	27	1.9E-03	6.7E+00	1.7E+00	2.8E-01	7.3E+00	1.1E+01
Kent Senior Center	07/19/12	22	3.5E-01	1.6E-01	3.8E-01	8.7E-02	3.6E-01	2.2E-01
Kent Senior Center	07/26/12	7	6.1E-01	1.7E-01	2.4E-02	2.5E-01	7.8E-01	2.7E-01
Kent Senior Center	08/16/12	21	1.2E+00	6.7E-01	6.2E-01	4.1E-01	2.1E-01	5.8E-01
Kent Senior Center	09/06/12	21	1.8E-01	3.0E-01	8.0E-01	7.2E-02	6.3E-01	1.0E+00
Kent Senior Center	10/24/12	14	1.2E-03	3.9E-02	1.1E-01	8.8E-01	8.7E-01	1.0E+00
Kent	08/25/11	29	2.0E-01	2.0E-01	5.8E-01	1.3E-01	5.7E-01	9.3E-01
Kent	09/29/11	8	1.5E-04	2.9E-01	5.4E-03	7.7E-01	3.7E+00	1.9E+00
Kent	09/29/11	8	8.1E-01	3.0E-01	2.4E-02	4.5E-01	2.3E+00	2.2E+00

Site	end date	sampling period (days)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Kent	10/19/11	20	1.5E-02	4.9E-03	8.0E-04	1.8E+00	1.6E-03	1.1E-02
Kent	10/19/11	20	5.0E-04	1.3E-02	7.9E-03	2.1E+00	4.6E-03	8.1E-02
Kent	11/16/11	14	6.0E-01	5.3E-01	1.9E-02	1.5E-01	2.0E+00	1.1E+00
Kent	03/06/12	13	8.1E-01	5.0E-01	9.6E-02	2.6E-01	1.2E+00	1.5E+00
Kent	07/19/12	22	1.8E-01	1.3E-01	3.9E-01	8.2E-02	5.4E-01	4.5E-01
Kent	07/26/12	7	3.3E-01	2.7E-04	1.5E-03	2.6E-01	1.1E-01	5.3E-01
Kent	08/16/12	21	1.4E-01	2.8E-01	1.0E+00	6.9E-02	1.1E+00	1.1E+00
Kent	09/06/12	21	4.4E-01	5.7E-01	1.2E+00	7.4E-02	1.1E+00	1.5E+00
Kent	10/24/12	14	5.8E-02	1.8E-03	7.4E-02	2.0E+00	2.7E+00	9.3E-01
Enumclaw	12/28/11	29	4.5E-01	1.0E+00	5.6E-01	1.8E-02	8.9E-01	2.0E-01
Enumclaw	02/07/12	14	1.2E-01	6.9E-02	1.2E-02	2.6E-01	2.2E-01	3.2E-03
Enumclaw	06/25/12	25	5.0E-01	1.6E-03	5.5E-02	2.4E-01	9.1E-02	1.0E-03
Enumclaw	07/19/12	24	5.5E-01	5.7E-04	4.7E-03	1.6E-01	2.2E-01	9.2E-03
Enumclaw	07/26/12	7	2.9E-01	4.4E-04	3.6E-02	2.0E-01	1.8E-01	1.5E-02
Enumclaw	08/16/12	21	1.9E-01	1.8E-01	1.9E-01	7.9E-02	1.1E+00	4.2E-04
Enumclaw	08/27/12	10	1.6E-01	9.5E-02	1.6E-01	7.0E-02	4.5E-01	3.1E-04
South Park	08/25/11	29	5.5E+00	3.4E+00	5.7E-01	8.3E-01	2.8E+00	3.0E+00
South Park	09/29/11	8	5.7E+00	5.3E+00	9.4E-03	7.3E-01	6.3E+00	2.8E+00
South Park	10/19/11	20	2.5E+00	2.3E+00	2.4E-03	1.0E+00	5.6E+00	2.6E+00
South Park	12/28/11	29	4.4E-01	9.4E-01	4.0E-01	1.7E-01	3.4E+00	1.1E+00
South Park	02/07/12	14	5.2E+00	4.4E+00	4.9E-03	4.8E-01	3.5E+00	2.5E+00
South Park	03/29/12	14	6.2E-01	1.1E+00	2.4E-01	6.4E-01	2.4E+00	1.8E-01
South Park	07/26/12	7	2.4E+00	1.1E+00	2.3E-01	1.1E-02	1.6E+00	1.7E+00
South Park	08/16/12	21	7.2E+00	6.7E+00	1.2E+00	4.7E-01	9.0E+00	4.2E+00
South Park	09/06/12	21	4.7E+00	2.2E+00	2.2E+00	7.0E-01	9.5E-01	3.5E+00
South Park	10/10/12	27	3.8E+00	2.9E+00	1.2E+00	4.7E-01	3.6E+00	5.1E+00
Duwamish/Diagonal	04/25/13	15	6.5E-01	9.7E-01	1.4E+00	1.8E-01	1.4E+00	2.1E+00

Site	end date	sampling period (days)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Duwamish/Diagonal	05/09/13	14	3.1E+00	5.4E+00	8.2E+00	4.3E-03	1.5E+01	2.0E+01
Duwamish/Diagonal	08/01/13	30	1.8E-01	1.3E-01	7.7E-01	7.1E-02	3.6E-01	1.0E+00
Duwamish/Diagonal	10/31/13	14	9.3E-01	2.2E+00	9.8E-01	8.2E-04	6.2E+00	4.9E+00
Duwamish/Diagonal	11/14/13	14	1.8E+00	1.3E+00	1.0E+00	1.2E+00	9.6E+00	3.8E+00
South Park	04/25/13	15	1.8E+00	1.9E+00	1.0E+00	2.9E-01	1.7E+00	2.4E+00
South Park	05/09/13	14	2.5E+00	3.8E+00	3.7E-01	9.1E-04	1.7E+00	1.6E+00
South Park	08/01/13	30	1.2E+00	7.9E-01	4.7E-01	2.3E-01	1.3E+00	1.1E+00
South Park	10/31/13	14	7.8E+00	3.7E+00	4.5E-01	2.4E-01	3.0E+00	8.4E+00
South Park	11/14/13	14	2.3E+01	1.4E+01	6.9E-01	4.4E+00	1.1E-02	2.8E+01
Georgetown	04/25/13	15	1.6E+01	2.0E+01	9.9E-01	4.3E-01	1.2E+01	1.1E+01
Georgetown	05/09/13	14	6.2E+01	4.5E+01	3.6E+01	1.7E+00	1.4E-01	3.1E+01
Georgetown	08/01/13	30	1.6E+01	1.1E+01	9.5E-01	1.9E+00	1.2E+00	3.2E-03
Georgetown	10/31/13	14	2.8E+01	2.1E+01	1.3E+00	7.5E-01	3.2E+00	1.5E+01
Georgetown	11/14/13	14	1.9E+00	1.5E+00	7.6E-01	8.0E-01	1.7E+00	2.0E+00
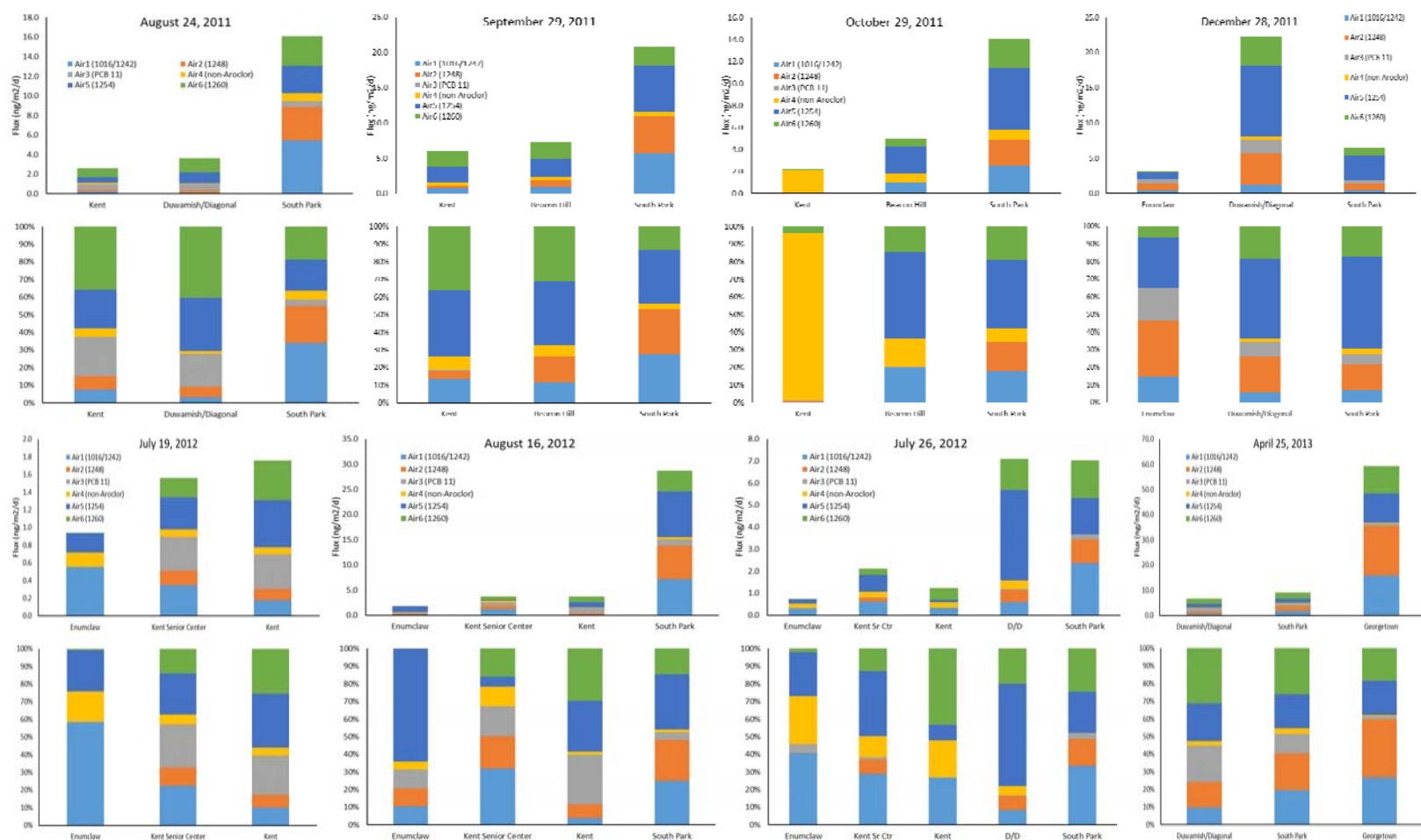
Figure S-1. Synoptic sampling. Each pair of bar charts represents one sampling event at multiple locations, with the end date of the sampling period is given at the top. In each pair of bar charts, the top panel shows the fluxes attributed by the PMF model to each of the six factors in units of ng m^{-2} d^{-1}, and the bottom panel shows the factors as a percent of total in that sample.

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